

COST-EFFECTIVENESS RELATIONSHIPS FOR THE REMOVAL
OF CADMIUM, MERCURY, AND CYANIDE FROM INDUSTRIAL WASTESTREAMS

Preliminary Analysis

For
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Scope of the Investigation

The objective of this work was to estimate the cost of removing cyanide, mercury, and cadmium from industrial wastes and to obtain estimates of the residual concentrations which can be obtained using best available treatment. Because estimates were assembled from readily available literature data and from communication with researchers and equipment manufacturers, the values used in this report cannot be taken as the most accurate estimates available. Considerable more time in evaluating data from all sources would be required to arrive at final judgements. Treatment costs were obtained from industrial waste treatment cost relationships, costs for municipal wastewater treatment processes, and from the best judgement of equipment manufacturers. In many cases it was necessary to use attainable effluent concentrations given by researchers and equipment manufacturers without having access to the detailed conditions under which the results were obtained.

Several assumptions were made regarding the wastestream to be treated. These conditions may be enumerated as follows:

1. Waste flow = 3 mgd.
2. Influent concentrations of the species of concern = 2 mg/l.
3. Waste constituents to be removed can not be isolated in more concentrated streams. Therefore, it was assumed necessary to

treat the entire waste flow.

4. The wastestream would contain some suspended solids and organic constituents not removed in upstream treatment processes.
5. The effect of complexing agents could not be thoroughly considered due to lack of applicable information.

Analytical Limits of Detection

In order to add perspective to the residual concentrations of these toxic substances reported, the limits of detection for each constituent were reviewed. Briefly, the findings are as follows:

1. Mercury. The flameless atomic absorption procedure recommended by the EPA is capable of detecting mercury at the 0.01 ppb level; EPA, however, recommends that 0.2 ppb be set as the practical detection limit for mercury in natural waters.
2. Cadmium. The detection limit for cadmium in water when determined by flame atomic absorption at 228.8 nm is about 40 ppb, using the Boling burner as recommended in Standard Methods (13th Ed). An adaptation known as the Delves cup method, which involves analysis of evaporated samples, permits detection limits for blood samples (and presumably for wastewater samples) of approximately 2 ppb. Methods based on atomic fluorescence and neutron activation are capable of detection limits several orders of magnitude lower, but their suitability for wastewater analysis has not been established.
3. Cyanide. The most sensitive practical methods for cyanide are colorimetric. The procedure suggested by Standard Methods involves conversion

of cyanide from a distilled sample to cyanogen chloride, which then reacts with a pyridine-pyrazolone reagent to form a blue dye. The latter is determined spectrophotometrically at 620 nm. Standard Methods gives the effective range as 1 - 5 µg in the wastewater; this would correspond to 40 - 200 ppb, depending on how the sample was prepared. A five-fold increase in sensitivity is said to be achieved by extracting the dye with butyl alcohol.

Treatment Processes

Treatment processes which were considered for the removal of each ion are discussed below. This discussion is limited to process parameters which have the greatest effect on treatment performance.

A. Cadmium

1. Precipitation. Precipitation of Ca(OH)_2 by lime treatment at pH 11 is expected to reduce the cadmium concentration from 2.0 mg/l to about 0.2 mg/l. The lime dose, which depends on the waste alkalinity, was estimated at 400 mg/l. The effluent pH was readjusted to 7 - 8 by recarbonation. Sludge production was estimated at 500 mg/l.
2. Precipitation and Filtration. The precipitated and settled effluent was applied to a granular media filter where the cadmium concentration is further reduced from 0.2 mg/l to about 0.02 mg/l. This removal was based on data from the treatment of municipal wastes containing similar cadmium concentrations. No specific data for the treatment of industrial wastes was available.

3. Ion Exchange. Cadmium can be removed to less than 10 ppb with ion exchange. A resin which is selective for cadmium or a mixed bed resin can be used. However, the mixed bed process is more practical. There are several types of resins which could be utilized including carboxylic acid resins and chelating resins. In this case, a chelating resin may be better because of the low salt splitting capacity. The degree of removal and the type of resin utilized is dependent on the complex being removed.

4. Reverse Osmosis. Generally, 97 to 99 percent rejection of cadmium can be obtained by reverse osmosis in a single-stage process. However, in this application, because of the low influent concentration assumed, i.e., 2 ppm, imperfections in the membrane, would result in a lower percent rejection. Because of the higher surface area and wider operational pH range, hollow fiber membranes would be recommended.

5. Activated Carbon. Cadmium levels of <50 ppb are obtainable by the use of activated carbon. Although these low levels are achievable, the carbon loading is very low, i.e., 3 lb Cd/100 lb carbon. A residence time of 35 to 40 minutes is required for good removal.

B. Mercury

1. Lime Precipitation. Precipitation of mercuric oxide by lime treatment at pH 11 is expected to reduce the mercury concentration from 2 mg/l to 0.4 mg/l. The lime dose was estimated at 400 mg/l for waste with 200 mg/l alkalinity as CaCO_3 . The effluent pH must be readjusted to 7 - 8 by recarbonation. Sludge production was estimated at 500 mg/l.

2. Sulfide Precipitation and Precoat Filtration. Precipitation of mercuric sulfide by adding a sulfide source such as sodium hydro-sulfide followed by precoat filtration can reduce mercury concentrations from 2.0 mg/l to 0.03 mg/l. This information was obtained from an existing pilot plant treating a chlor-alkali industrial waste. In the absence of other sulfide consuming compounds, the sulfide dose was estimated to be 10 mg/l in excess of the stoichiometric requirement, i.e., about 18 mg/l of NaHS for 2 mg/l mercury. The excess sulfide was then precipitated as FeS by adding ferrus sulfate (about 75 mg/l).
3. Ion Exchange. Mercury can be removed to approximately 10 ppb by ion exchange. Again, as in the case of cadmium, the type of resin employed depends on the metal complex to be removed and the other constituents in the wastewater.
4. Reverse Osmosis. A 95 to 97 percent rejection of mercury can be obtained by a single-stage reverse osmosis system assuming the mercury is in the proper form. The complexed metal or free ion is rejected; however, organic mercury would not be rejected. Again, this percent rejection may be lower, due to membrane imperfections at these low levels. The hollow fiber membrane would also tend to give better results in this application because of the larger specific surface and wider pH range.
5. Activated Carbon. Mercury levels of 1 to 5 ppb have been reported from the treatment of chlor-alkali wastes. However, effluent levels of 34 ppb were obtained in a study with municipal wastes. Again, the

carbon loading is low, i.e., 3 lb Hg/100 lb carbon. The adsorbability of mercury varies significantly with pH with the best results obtained at pH 4 to 6. The adjustment of pH with HCl enhances removals probably due to the precipitation of Hg Cl_2 . The current facilities which utilize activated carbon for mercury removal do so on a "throw-away" basis. When regenerating carbon with heat or hot gases, problems develop with mercury vapors.

C. Cyanides

1. Alkaline Chlorination. Cyanides are completely oxidized to N_2 and carbonates in a two-stage process by adding caustic soda and chlorine. Excess chlorine is reduced by the addition of SO_2 . The process is carried out in a continuous flow system with the chemicals being fed automatically through pH and ORP control units. For a cyanide concentration of 2 mg/l the chemical doses are estimated as follows: Cl_2 - 20 mg/l, NaOH - 25 mg/l, and SO_2 - 5 mg/l. Effluent concentration of cyanide is reported as 0 with the analytical method used. For the present calculations a conservative value of 0.2 mg/l was assumed. (See section on analytical method for a more detailed discussion of detectable limits.)

2. Ion Exchange. Free cyanide can be removed to 10 ppb by the use of a strong base anion exchanger. Again, various resins can be employed. Removals are affected by the presence of cyanide in complexed forms.

3. Activated Carbon. Cyanide can be removed to 50 ppb by the use of activated carbon. The process involved is catalytic oxidation with

CuSO_4 and oxygen which converts the cyanide to CO_2 and N_2 . One disadvantage associated with this process is that copper appears in the effluent in concentrations up to 0.1 ppm. The copper is capable of displacing the majority of the heavy metals which are complexed with cyanide but copper is not capable of displacing the iron. Therefore, any iron which is in the wastewater must be removed prior to the carbon system. Removal of iron was not considered in this investigation. To prevent the formation of metal hydroxides and subsequent filter clogging, the pH of the influent stream must be between 6.5 and 8. While this process appears to be a feasible method for treating cyanide-bearing wastes, the technological success of the process has not been fully established.

4. Ozonation. Cyanide can be removed to less than 10 ppb with ozone alone if the cyanide is not complexed with iron. However, if the cyanide is complexed, pH control and heat or ultraviolet light must be employed in combination with the ozone for adequate cyanide removal.

Treatment Costs

All cost estimates were adjusted to January 1972 levels (EPA Sewage Treatment Plant Index = 175). Allowances were made for engineering, legal, and administrative fees and miscellaneous construction costs. Special conditions assumed for each process are discussed below.

1. Precipitation and Filtration. Costs were estimated for one-stage precipitation processes. Sludge handling was estimated using gravity thickening and vacuum filtration. The sulfide precipitation process

included NaHS addition, filtration through a diatomaceous earth filter, Fe SO_4 addition, flocculation, and sedimentation.

2. Oxidation Processes. Facilities for cyanide removal by alkaline chlorination and ozonation included flocculation basins and chemical feed facilities. For chlorination the conventional two-step process was used which employs pH and ORP controls; additional facilities were added for dechlorination using SO_2 .

3. Reverse Osmosis. Reverse osmosis was used for the removal of cadmium and mercury. Cyanide may be removed if present as CN^- or cyanide complexes: however, it appears that any unionized HCN can pass through membranes. All capital and operating costs were obtained from manufacturers based on "best judgement" estimates of costs to achieve the given residual metals concentrations. Filtration costs were also added for pretreatment in all cases. Because cost data are not from independently reported sources, the adequacy of membrane cleaning and replacement costs cannot be determined. It is possible that higher costs might be obtained upon application of this process to specific wastestreams; however, no basis exists for increased costs in this investigation.

4. Ion Exchange. Ion exchange costs were estimated from manufacturer's data using the "0.6 rule" to make adjustments in plant capacities. Pretreatment included activated carbon and filtration, although this pretreatment might not be necessary for all wastes. Due to lack of

data and the complexity of selecting operating parameters, these costs are speculative.

5. Activated Carbon. Metal removal results and costs using activated carbon were estimated from one reported investigation as interpreted by two carbon manufacturers. Acid washing of spent carbon was included to restore the metals capacity of the carbon. An additional 10 percent was added to O&M costs to cover the purchase of acid. No costs were added for thermal regeneration to destroy organics which would adsorb to the resin. However, it was assumed that carbon would be completely replaced twice per year. Costs for the catalytic destruction of cyanide were based on the process developed by Calgon Corporation. No facilities for iron removal prior to this process were assumed. When iron is present, this process might not be feasible. Although the treatment costs using activated carbon in all cases are attractive, it is felt that the technical feasibility of these processes has not been proven and therefore, that costs are somewhat speculative. Attainable effluent levels for mercury which have been reported varied from 1 - 5 ppb to 54 ppb. This range is indicated in the cost-effectiveness relationship. However, the lower residual values are subject to question.

Cost effectiveness relationships are shown in Figure 1 - 3.

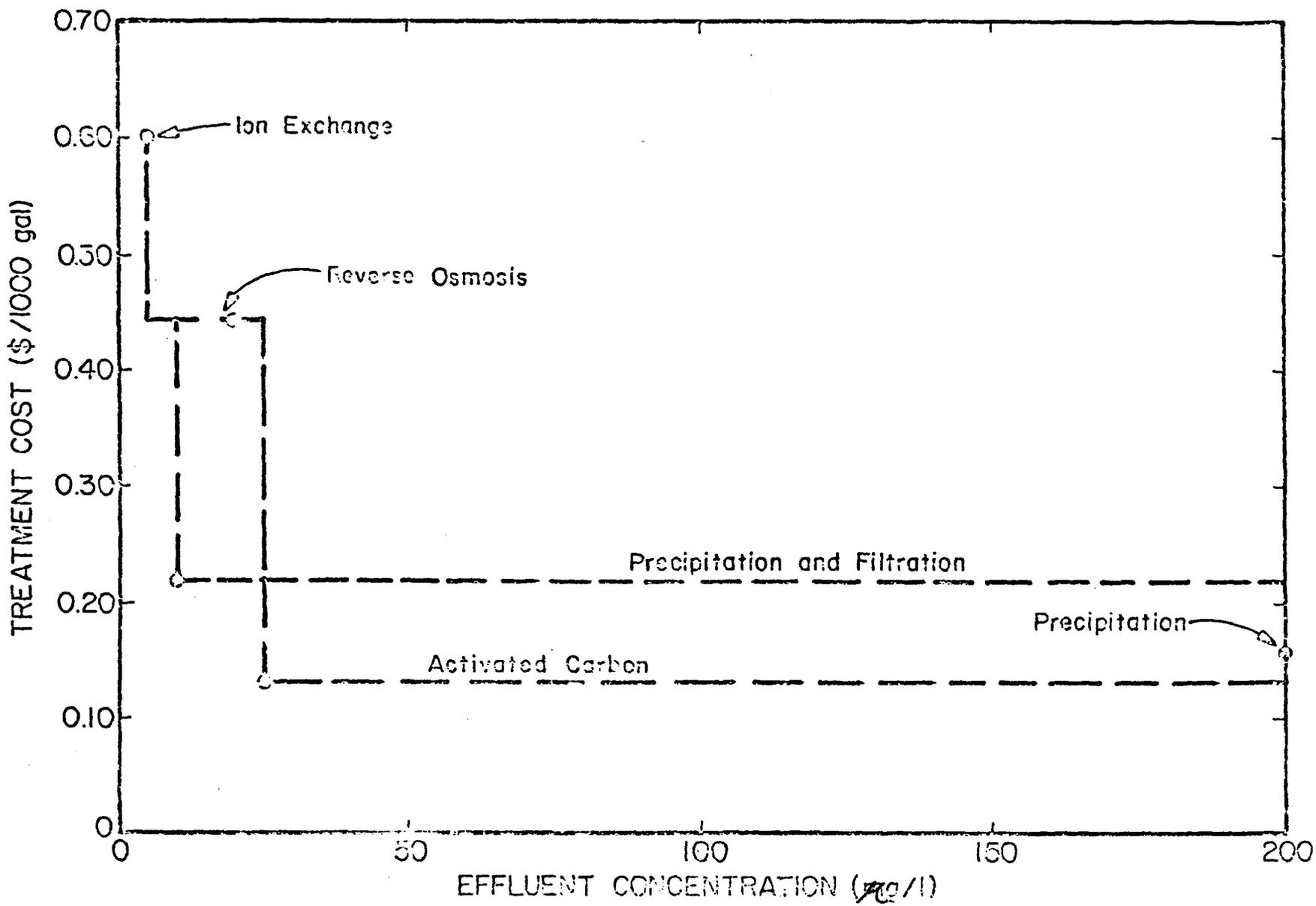


FIG. 1. COST-EFFECTIVENESS RELATIONSHIP FOR CADMIUM REMOVAL

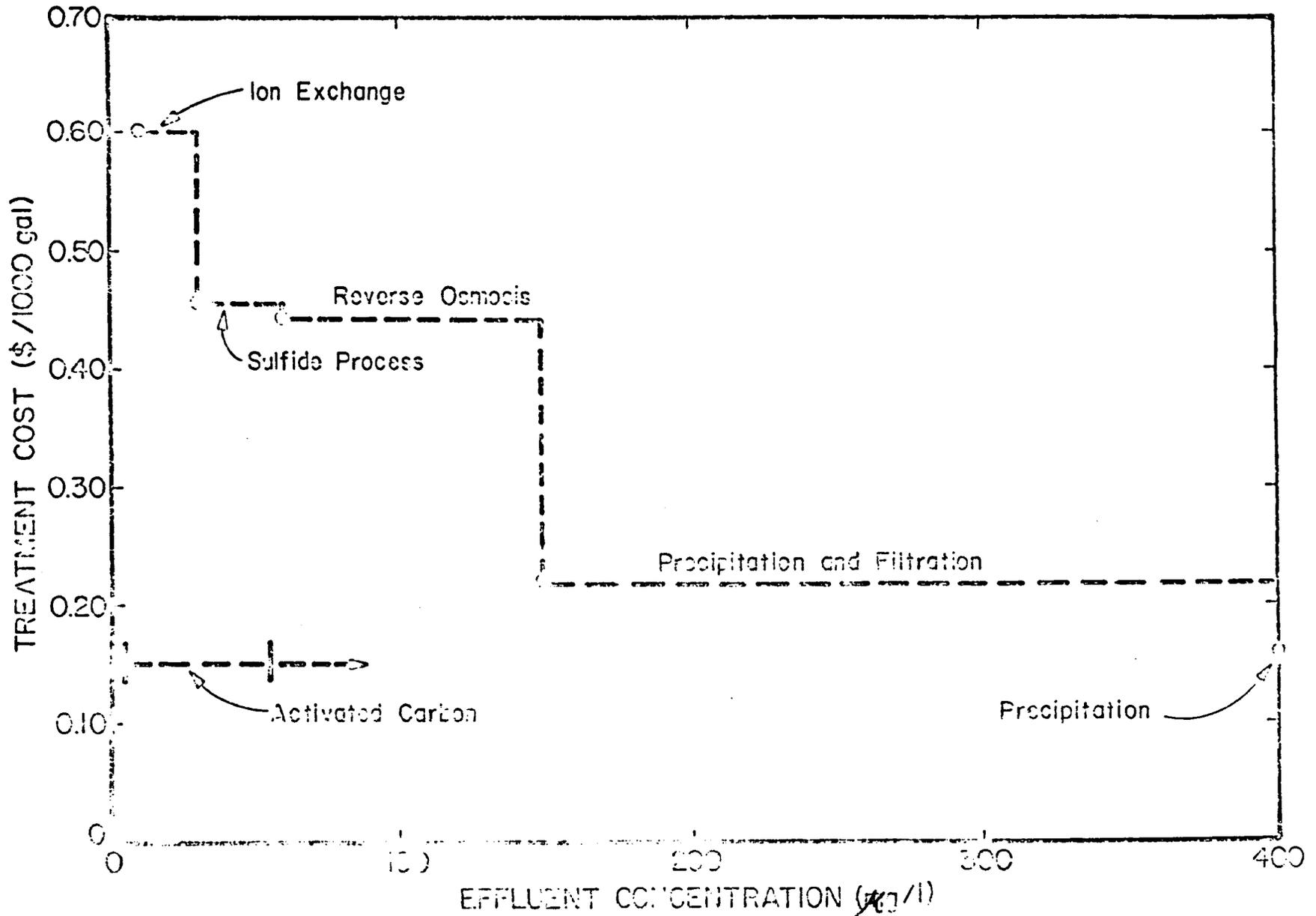


FIG. 2. COST-EFFECTIVENESS RELATIONSHIP FOR MERCURY RE -
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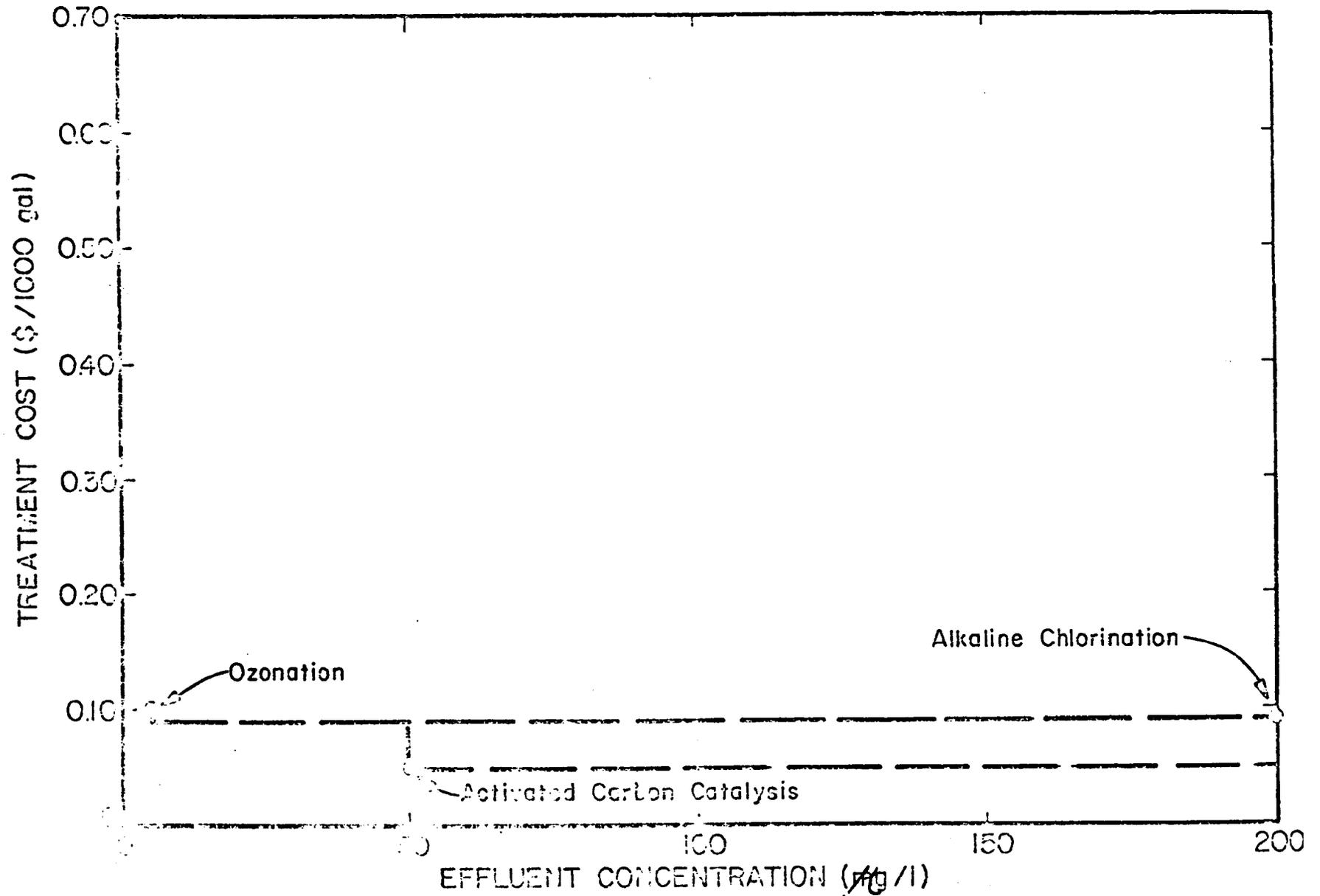


FIG. 3. COST-EFFECTIVENESS RELATIONSHIP FOR CYANIDE REMOVAL